COMPOSITION OF A LOW-TEMPERATURE BITUMINOUS COAL TAR

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INTRODUCTION

A true low-temperature coal tar is generally defined as that tar produced by carbonizing coal at a temperature not exceeding 500°C. The one outstanding chemical characteristic of a true low-temperature coal tar is the small amount of any individual compound, similar in nature to petroleum and shale oil, and quite different from coke-oven tar in which a single compound, such as naphthalene can account for as much as 10 percent of the tar.

Detailed characterization of low-temperature tars has received little attention until the last few years. Representative of the excellent research being conducted in this field is that of McNeil of the Coal Tar Research Association, Landa of Czechoslovakia, Kalechits and Kuznetsov of Russia, Jäger and Kattwinkel of Germany, Kikkawa and associates of Japan, Kahler and co-workers of Battelle Memorial Institute, Vahrman of Northampton College of Applied Technology, Parant of France, and Brown of Australia. It is outside the scope of this report to review the research of these investigators. The purpose of this paper is to summarize the research carried out by the U.S. Bureau of Mines on a particular low-temperature bituminous coal tar.

The main reason for identifying and determining the amounts of individual compounds in a low-temperature coal tar is to obtain a true picture of the chemical nature of the tar so that refining and utilization can then be approached from a logical standpoint. By this it is not implied that refining will necessarily consist of isolating individual compounds on a commercial scale. However, the results from such studies may indicate that the refining of low-temperature tars will require the development and application of a partly different set of chemical processes to suit the special chemical nature of these tars.

TAR ACIDS

Analytical Procedures and Results

The tar used in this work was made from Arkwright (W. Va.) Pittsburgh-seam, high-volatile bituminous coal in a fluidized carbonization pilot plant at 500°C. The raw tar was de-ashed, dehydrated, and topped to 175°C at the plant. The tar was distilled under very mild temperature conditions, 125°C at a pressure of 133 microns, so as to minimize structural alterations of tar components. For this purpose a rotary vacuum stripper was used. Under these

conditions of distillation, the distillate amounted to about 21 weight-percent of the tar. The tar acids were recovered from the distillate by a Claisen alkali extraction using the procedure of Woolfolk and his associates (19).* The extracted phenols represented 3.54 weight-percent of the tar.

Low-Boiling Tar Acids. The phenols recovered from the distillate were fractionated in a Piros-Glover** micro spinning band still. The mixture of tar acids boiling up to 234°C (at atmospheric pressure) was fractionated in a Perkin-Elmer model 154 chromatographic apparatus using a 12-ft column of 1/4-in. copper tubing packed with Johns-Manville C-22 firebrick, 30 to 60 mesh, containing 34.7 weight-percent di-n-octyl phthalate. The column temperature was 160°C and a carrier-gas flow rate of 150 cc helium per minute was used. The results are shown in Figure 1. Thirteen peaks, or shoulders on peaks were obvious, indicating a minimum of thirteen phenols. Retention times of the substances producing the peaks, relative to peak 1, were determined and compared with the relative retention times of individual pure phenols.

A collecting system, based on one recently described (13), was used to advantage in identifying the components in peaks that were incompletely resolved. By using the collecting system, followed by infrared analysis, identities of the phenols producing the various peaks were confirmed in nearly all instances. By the combination of retention times, infrared analysis of fractions containing more than one phenol, and the peak areas, a reasonably good analysis of a total tar acid mixture boiling up to 234°C was obtained.

High-Boiling Tar Acids. To complete the characterization of the tar acids it was necessary to fractionate and analyze the high-boiling phenols. The method chosen for this complex material was countercurrent distribution, supplemented by ultraviolet and infrared spectrophotometry.

A 200-g portion of tar acids from the tar distillate was distilled at 20 mm through a column filled with glass helices. All the material boiling up to 118° head temperature, equivalent to about 232° at 760 mm, was removed as a single fraction, leaving a residue of 50 g high-boiling phenols or 25 weight percent of the original tar acid mixture. A charge of 41.68 g high-boiling tar acids was distilled at 2.9 mm and a reflux ratio of 20 to 1 in a spinning band still. The infrared spectra were obtained on all of these fractions; they were then combined on the basis of qualitative similarity to give 10 samples and subsequently fractionated by countercurrent distribution, except for the lowest boiling ones.

The instrument used was a 60-tube all-glass model, with 200 tubes in the fraction collector and an automatic robot mechanism. The tube capacity for each phase was 40 ml. The instrument was operated to give 100 to 105 transfers or plates. The average sample size was about 185 mg; the upper phase consisted

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of spectro-grade cyclohexane, and the lower phase was a phosphate buffer made from different proportions of 0.5M Na_3PO_4 and 0.5M Na_2HPO_4 to vary the pH from 9.94 to 11.36.   A particular value was chosen because of the suspected presence of certain phenols and their known partition coefficients.   After the completion of each fractionation, 8 ml of 1 to 1 hydrochloric acid was added to the tube to neutralize the buffer and mixed well to dissolve the phenols in the cyclohexane.

Ultraviolet spectra were obtained on each cyclohexane solution, and plots were prepared of total absorbance at two informative wavelengths versus tube number. A typical curve is shown in the upper half of Figure 2. On the basis of these plots and the qualitative similarity of the ultraviolet spectra, combinations of the cyclohexane solutions were made for infrared analysis.

On the basis of the combined qualitative results of the ultraviolet and infrared spectra, the constituents from each countercurrent distribution fractionation were distinguished and assigned numbers.   The distribution curve of each constituent was readily visualized by following the appearance and disappearance of characteristic absorption bands in the spectra of consecutive countercurrent fractions.   This was made easier by the fact that the distributions are essentially Gaussian as well as symmetrical. Distribution peaks observed in this manner always coincided with peaks in the plot of total absorbance versus tube number.

The milligrams of each phenol in each tube were determined from the absorptivities at characteristic wavelengths, as obtained from authentic specimens or literature data.   Where such absorptivities were not available, an average absorptivity was obtained from phenols with the most similar structure or, for constituents of unknown structure, from phenols with the most similar absorption bands and boiling points.   Plots of milligrams versus tube number were prepared (see bottom half of fig. 2).

Nature of Tar Acids

The results of the qualitative and quantitative analytical procedures for the tar acids are summarized in Table 1.   The compounds have been arranged in this table according to groups involving the same fundamental ring structures. Approximately 80 individual compounds were identified, mostly with respect to individual isomers, and the amounts were determined, or estimated, in nearly all instances.

Five different fundamental ring structures were observed among the tar acids.   These were:

1. Phenol   4. Naphthol and Tetrahydronaphthol
2. Indanol and Indenol   5. Fluorenol
3. Phenylphenol

In addition, aliphatic carboxylic acids were present in all boiling ranges, and indanones were present as impurities in a few fractions.   The latter were apparently capable of functioning as acids in alkaline solutions, probably through

a keto-enol mechanism. Polyhydric phenols were not present in large enough quantities to detect. As these compounds are quite soluble in the warm discharge water, they were probably effectively extracted from the tar at the plant.

The individual tar acids identified consisted of these seven fundamental structures; mostly methyl groups and some ethyl groups were attached. About 3 tar acids had isopropyl groups, and about 10 had n-propyl groups, but no phenols with butyl groups or higher could be found. Cyclohexyl groups and probably also cycloalkenyl groups were present. A small proportion of alkenyl groups, like propenyl, were likewise present. Alkylphenols with a total of more than 6 carbon atoms in alkyl groups were apparently absent. The most prevalent class of phenol among the high-boiling tar acids was the naphthols.

Nine individual tar acids were identified; each comprised more than 3 weight-percent of the total tar acids and together comprised nearly one-half of the total tar acids. All were low-molecular-weight alkylphenols, as follows: o-, m-, and p-cresol, 2,4-, 2,5-, 3,4-, and 3,5-xylenol, 2,3,5-trimethylphenol, and 4-ethyl-2-methylphenol.

Complete details of the characterization of the tar acids have been published (10, 11, 12, 15, 16, 20).

TAR BASES

Analytical Procedures and Results

About 3 liters of the low-temperature bituminous coal tar distillate were extracted by the method of Fisher and Eisner (6) to remove tar bases. The tar bases were purified by treatment with solid potassium hydroxide to pH 12, extraction with ether, acidification of the ether extract with sulfuric acid, evaporation of the ether by streaming nitrogen at room temperature, regeneration by adding solid potassium hydroxide to pH 12, extraction with benzene and drying the extract by refluxing under nitrogen in a Dean-Stark apparatus. Distillative removal of the benzene yielded about 40 g dry tar bases, representing about 0.31 weight-percent of the total tar.

A 37.50-g portion of the dry tar bases was fractionated in a Piros-Glover micro spinning band still, using a reflux ratio of 15 to 1, a kettle temperature of about 25° to 186°C, and a head pressure of 80 to 3 mm from the beginning to the end of the run, respectively. Infrared spectra of the tar-base distillate fractions were obtained with a model 21 Perkin-Elmer infrared spectrophotometer and ultraviolet spectra with the Beckman DK-2 spectrophotometer.

These spectra were compared with those of individual compounds that conceivably could be present in the various fractions on the basis of boiling point. The compounds found in the distillate fractions are listed in Table 2. The compounds have been arranged according to groups involving the same fundamental ring structures. Approximately 50 individual compounds were identified, and the amounts were determined, or estimated, in nearly all instances.

Nature of Tar Bases

Eight different fundamental ring structures were observed among the tar
bases. These were:

1. Pyridine   5. Benzoquinoline
2. Cyclopentenopyridine   6. Aniline
3. Phenylpyridine   7. N-benzylaniline
4. Quinoline   8. Naphthylamine

Two ring structures appeared to be present, although no individual compounds
could be identified; these were tetrahydroquinoline and phenylaniline. A special
effort was made to identify isoquinoline and its alkyl derivatives, but no indication
of their presence was found. These structures covered the boiling range from
initial boiling point to about 355°C. It would appear to be certain that the poly-
cyclic structures also would be present in the distillation residue or "pitch."

The individual tar bases identified consist of these eight fundamental
structures, with mostly methyl and some ethyl groups attached. One compound
with an isopropyl group was identified, but no alkyl groups with chain lengths
greater than two carbon atoms were observed. Under the conditions of formation
of the tar (500°C), alkyl chains of three or four carbons could conceivably
cyclize to form fused saturated rings, as exemplified by cyclopentenopyridines
and tetrahydroquinolines. The spectra of alkyl derivatives of these compounds
were not available but 2,3-cyclopentenopyridine was definitely identified, and
tar-base-distillate fractions 10 to 20 appeared to contain appreciable amounts of
alkyl-5,6,7,8-tetrahydroquinolines. There was no doubt, from the ultraviolet
spectra of these fractions, that they were rich in some kind of pyridine, that is,
compounds with a pyridine ring but no other unsaturated ring in the molecule.
Yet the boiling range of these fractions was above the boiling points of the known
highly alkylated pyridines. On the other hand, the boiling points of the known
alkyl-5,6,7,8-tetrahydroquinolines, which have a pyridine ring but no other aro-
matic ring, covered the boiling range for fractions 10 to 20 quite closely.

Eight individual tar-base compounds were identified; each comprised
more than two weight-percent of the total tar bases and together they comprised
fully one-fourth of the total tar bases. All were quinolines, as follows: 2- and
4-methylquinoline, 2,4-dimethylquinoline, 2,4,6-, 2,4,7-, 2,4,8-, and 2,6,8-
trimethylquinoline, and benzo[f]quinoline. From this standpoint one can say that
quinolines, especially those alkylated in the 2- and 4-positions, are the com-
pounds that best typify the tar bases from low-temperature bituminous coal tar
and not pyridines, as might have been assumed.

Details of the characterization of the tar bases, including infrared
spectral-structural correlations of quinolines, have been published (4, 13, 17).

NEUTRAL OIL

Analytical Procedures and Results

The neutral oil, free of tar acids and bases, was fractionally distilled
into 66 fractions. The silica gel adsorption method based on displacement
chromatographic techniques, which have been applied to petroleum distillates (7)

and shale-oil naphthas (5), was adapted for separating the aromatic hydrocarbons from saturates and unsaturates. Results of the displacement chromatographic separation are given in Table 3.

Aromatic Hydrocarbons. Aromatic hydrocarbons in the distillate fractions boiling up to 275°C were analyzed by gas-liquid chromatography.

Generally, two methods were followed to identify the aromatic hydrocarbons. The first consisted of (a) preliminary identification of the unknown by comparing its retention time with those of known compounds, and (b) final confirmation of the identity by comparing the infrared spectrum of the collected material with that of the authentic specimen. The chromatograms for two different aromatic cuts, shown in Figure 3, illustrate a good separation in (A) and a complete overlapping of some components in (B), which were subsequently identified and their ratios estimated by infrared spectrophotometry. Table 4 shows the results of the identifications, the peak numbers in the table corresponding to the peak numbers in Fig. 3.

The second method of identification involved the correlation curves of relative retention and boiling points, which were applied in those instances where retention times of authentic specimens were not available.

The aromatic hydrocarbons found in the low-temperature bituminous coal tar and their quantities are presented in Table 5.

Analysis of the aromatic hydrocarbons in the distillate fractions boiling from 275° to 344° is in progress. They are being analyzed by countercurrent distribution using a dual solvent system of 90 weight-percent ethyl alcohol in water for the lower phase and isooctane for the upper phase. Two runs were made on distillate fractions covering the range 275°-282°C, 9 runs on distillate fractions covering the range 287°-344°C and 1 run on the distillate residue boiling above 344°C. In each run 120 transfers were made. Both ultraviolet and infrared spectra are presently being obtained on the contents of each of the 120 tubes. Results to date show that the polycyclic aromatics are essentially completely separated from the paraffins and the olefins, and that the aromatics are separated from each other to a considerable extent. Among the compounds identified are phenanthrene, anthracene, dibenzofuran, carbazole, 1-methyl-carbazole, α-olefins, β-branched α-olefins, and trans β (or higher) olefins.

Considerably more detail on the identification of the aromatic hydrocarbons has been described in two earlier publications (1, 2).

C_{10}-C_{16} n-Paraffins, Isoparaffins and α-Olefins. The non-aromatic hydrocarbon concentrates were obtained from the same neutral oil used in the work on aromatic hydrocarbons. The paraffins and olefins were analyzed by gas-liquid chromatography.

Identification of individual n-paraffins and α-olefins in the non-aromatic cuts was based primarily on retention time. Infrared spectra served mostly for simply confirming the general chemical types. With the exception of 2-methyl-decane, authentic specimens of the isoparaffins were not available, so that a somewhat different approach had to be used. It was observed that when the

logarithms of the relative retentions of C_{10} through C_{16} n-paraffins and α-olefins were plotted against their respective boiling points, two parallel, slightly curved lines were obtained. It was assumed that the curve for the 2-methylalkanes would likewise be parallel to the curves for the n-paraffins and α-olefins, and would pass through the one known point for 2-methyldecane. Figure 4 shows the curves for these three chemical types at 170° and 220°.

The individual n-paraffins, isoparaffins, and α-olefins found in the neutral oil, and their amounts, are presented in Table 6.

The quantities of total naphthenes and total trans-olefins were estimated to be only 2.5 percent and 0.5 percent, respectively, of the neutral oil. The quantities of total n-paraffins, total isoparaffins and total α-olefins, however, were determined to be 5.20 percent, 1.03 percent and 2.40 percent, respectively, of the neutral oil. Thus, about three-fourths of the saturates and olefins were made up of the 21 individual compounds that were identified.

Details of this work have been published (3).

PITCH RESINS

Analytical Procedures and Results

The resins from the pitch remaining after the low-temperature bituminous coal tar was distilled were characterized by ring analysis, infrared and ultra-violet spectra, and pyrolysis to structural units. Resins from lignite and sub-bituminous tars were also characterized and are included in this section.

Two different resins were isolated from each pitch: (1) a low molecular weight resin that was insoluble in petroleum ether (boiling range 100° to 115°) but soluble in benzene; (2) a medium molecular weight resin that was insoluble in benzene but soluble in quinoline. The physical properties of these resins are given in Table 7.

The n-d-M method (8) was used for ring analysis. The method is not directly applicable to high oxygen content samples such as coal tar resins since the substitution of an oxygen atom for a methylene group results in an increase in the refractive index and, in particular, in the density of a hydrocarbon. A modification of the n-d-M method was devised that made it possible to obtain acceptable ring analyses of high oxygen content samples (14). A method was also developed for determining the arrangement of rings in polynuclear compounds using the ring index (total rings per carbon atom, R/C) and the atomic hydrogen to carbon ratio (H/C) (9). Seven different series of aromatic ring arrangements were presented ranging from entirely linear structures like phenanthrene, picene, etc., (Series I) to highly globular structures like coronene (Series VII). Data on the number and arrangement of rings in the two low-temperature bituminous resins are given in Table 8.

The resins have four or five aromatic rings and two to six oxygen atoms per molecule. In addition, the lower molecular weight resin apparently has a linear arrangement of rings with one or two saturated rings, while the higher

molecular weight resin has a globular arrangement of rings with five to seven saturated rings. Substituents such as methyl groups, are apparently present, in particular on the lower molecular weight resin.

The infrared and ultraviolet spectra of the resins indicate the following general structure for all of the resins, some features being considerably better established than others. The resins are basically aromatic compounds with mostly isolated single aromatic rings and some clusters of two fused aromatic rings. Saturated rings, possibly including ether groups, probably complete the hydrocarbon skeleton. The major substituents are phenolic hydroxyl groups and, in particular, methyl groups. Most aromatic rings have at least two substituents; these are mostly either methyl groups or fused saturated rings or both. Alkyl substitution is greater for the lower molecular weight resins. Carbonyl groups are present; these are conjugated with either aromatic rings or olefinic groups or both. The hydroxyl groups and carbonyl groups are not on adjacent carbon atoms in at least the great majority of instances, and the carbonyl group is probably not present in a quinone unit.

Insofar as comparisons can be made, these observations are in complete agreement with structural features determined by ring analysis and molecular formula.

Structure determination of the resins was also made by combined pyrolysis and gas-liquid chromatography. The pyrolysis apparatus consisted of a small coil made from a 25.5-in. length of 28-gauge nichrome wire suspended in a stainless-steel chamber connected directly to a gas-liquid chromatographic unit by a short length of 1/8-in. stainless-steel tubing. The chamber, the connecting tubing, and a longer preheating section of tubing were all electrically heated to approximately the same temperature, which was a few degrees below the GLC column temperature. Helium carrier gas passed through the preheat section and the pyrolysis chamber into the column.

The GLC column consisted of a 20-ft length of 1/4-in. copper tubing filled with 75 g packing made from 25 percent Apiezon L grease on 30 to 60 mesh fire-brick. A column temperature of 220°C was used so that relatively high-boiling products, such as phenols and naphthalenes, would be readily detected if present. Gas-liquid chromatographic fractions were collected for infrared spectra.

The semi-solid fraction of the benzene soluble, petroleum ether insoluble resins from a West Virginia bituminous coal tar pitch and a Nugget, Wyoming, subbituminous pitch were pyrolyzed under identical conditions. The resins were pyrolyzed at 528°C in a chamber preheated to 175°C using a sealed glass tube technique. The procedure consisted of placing about 25 mg of the finely divided resin in a glass capillary tube that was then evacuated, sealed, and inserted in the coil. With this size sample and a setting of about 22.5 volts, the tube shattered at 8.4 seconds. The volatile pyrolysis products were swept immediately and directly into the GLC column by the stream of helium.

The chromatograms obtained with the subbituminous and bituminous resins are shown in Figures 5 and 6, respectively. The relative retentions of the pyrolysis products producing the peaks are compared with the relative retentions

of pure compounds in Tables 9 and 10. The relative amounts of pyrolysis products from the two different resins are compared in Table 11. Three compounds were found in the pyrolysis products of the bituminous pitch that were not present for the subbituminous resin. These were 2-methylpentane, 2,3,3-trimethylpentane, and 2,2,3,4-tetramethylpentane. On the other hand, the infrared absorption bands characteristic of different types of olefins, which were readily observed for the pyrolysis products of the subbituminous resin, were absent in the spectra of the pyrolysis products of the bituminous resin.

It can be seen from Table 11 that the proportion of branched paraffins to benzene is considerably less for the pyrolysis products of the bituminous resin than for the subbituminous resin. Also, the proportion of dimethylbenzene is less for the bituminous resin than for the subbituminous resin. These results indicate a lower proportion of saturated, fused multi-ring systems with quaternary carbons for the bituminous resin than for the subbituminous resin. The reason for the apparently complete absence of olefins in the pyrolysis products of the bituminous resin is not known.

A resin molecule containing as part of its structure a unit like 5,6,6a,7, 8,12b-hexahydro-6,7-dimethylbenzo[c]phenanthrene could conceivably split up (with, of course, transfer of hydrogen from other structural units) to form 2,3,4-trimethylpentane, as shown in Figure 7. Only those methyl groups required for the formation of 2,3,4-trimethylpentane are shown; additional methyl groups would be present, as determined in previous work. One of the benzene rings in this unit could be released as such, or both benzene rings could be incorporated in the formation of the pyrolysis residue or char. The fact that the resins are rich in oxygen (10 to 15 weight-percent) whereas no oxygen-containing organic compounds could be identified in the volatile pyrolysis products would indicate that the oxygen-containing units in the resin (primarily benzene rings with phenolic hydroxyl groups) are involved in char formation. Under these circumstances there would be a greater proportion of aliphatic compounds than aromatic compounds in the volatile products, such as was actually observed.

Although the pyrolysis results might appear unusual or unexpected, nevertheless the general structure of the resins indicated by these results is the same as that indicated by ring analysis (including ring arrangement), infrared spectra, and ultraviolet spectra.

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TABLE 1. - Summary of tar acids identified in a low-temperature bituminous coal tar and their amounts

Distillable tar acids	Weight-percent[1]	Distillable tar acids	Weight percent[1]
Phenol	2.3	2-Cyclohexylphenol	0.20
o-Cresol	5.6	2-Alkylcycloalkylphenol I	0.02
m-Cresol	7.2	2-Alkylcycloalkylphenol II	0.01
p-Cresol	4.9	Cycloalkenylphenol I (?)[2]	0.005
o-Ethylphenol	1.5	Cycloalkenylphenol II (?)	0.04
m-Ethylphenol	2.5	4-Indanol	0.53
p-Ethylphenol	2.5	5-Indanol	0.49
2,3-Xylenol	1.3	1-Methyl-5-indanol (?)	0.36
2,4-Xylenol	9.1	3-Methyl-4-indanol (?)	0.09
2,5-Xylenol	3.7	4-Methyl-1-indanone (?)	0.15
2,6-Xylenol	1.4	6-Methyl-1-indanone (?)	0.01
3,4-Xylenol	3.7	Alkyl indanone	0.03
3,5-Xylenol	5.9	6-Methyl-5-indanol (?)	0.005
2,3,5-Trimethylphenol	3.3	7-Methyl-5-indanol	0.10
2,3,6-Trimethylphenol	0.01	4-Indenol	0.03
2,4,6-Trimethylphenol	1.4	5-Indenol	0.27
3,4,5-Trimethylphenol	0.13	1-, 2-, or 3-Methyl-4-indenol	0.14
3-Ethyl-2-methylphenol	0.01	Methyl indenol	0.08
3-Ethyl-4-methylphenol	0.01	1-, 2-, or 3-Polyalkyl-4-indenol . . .	0.13
3-Ethyl-5-methylphenol	2.1	3,4-Dinuclearphenol	0.06
4-Ethyl-2-methylphenol	4.5	5,6,7,8-Tetrahydro-1-naphthol . . .	0.02
5-Ethyl-2-methylphenol	0.01	5,6,7,8-Tetrahydro-2-naphthol	0.02
2-n-Propylphenol	0.01	2-Phenylphenol	0.08
3-n-Propylphenol	0.01	3-Phenylphenol	0.03
4-n-Propylphenol	0.13	4-Phenylphenol	0.37
4-Isopropylphenol	0.01	1-Naphthol	0.20
2,3,5,6-Tetramethylphenol	0.04	2-Naphthol	1.54
3-Methyl-5-n-propylphenol (?)	0.29	1-Methyl-2-naphthol	0.02
2-Methyl-5-isopropylphenol	0.01	3-Methyl-2-naphthol (?)	0.008
2-Ethyl-6-n-propylphenol (?)	0.26	4-Methyl-1-naphthol	0.04
3-Ethyl-4-n-propylphenol (?)	0.12	4-Methyl-2-naphthol (?)	0.11
4-Ethyl-3-n-propylphenol (?)	0.24	6-Methyl-2-naphthol (?)	0.01
4-Isopropyl-3-n-propylphenol (?)	0.14	7-Methyl-2-naphthol (?)	0.05
2,4-Di-n-propylphenol (?)	0.13	8-Methyl-2-naphthol (?)	0.02
2,4- or 3,4-Dialkylphenol (?)	0.02	2-Ethyl-1-naphthol (?)	0.85
3-Methyl-2-propen-1-ylphenol (?)	0.003	2,5- or 2,7-Dimethyl-1-naphthol (?) .	0.008
Alkenylphenol I	0.005	2,6-Dimethyl-1-naphthol (?)	0.008
Alkenylphenol II	0.001	5,7-Dimethyl-1-naphthol (?)	0.05
Alkenylphenol III	0.03	Methyl-2,3-, or 4-fluorenol	0.06

1 The distillable tar acids constitute 3.62 weight-percent of the tar.
2 (?) indicates uncertainty as to which isomer is present.

TABLE 2. - Summary of tar bases identified in a low-temperature bituminous coal tar and their amounts

Distillable tar bases	Weight-percent[1]	Distillable tar bases	Weight-percent[1]
Aniline	0.26	N-Benzyl-2-methylaniline	0.19
3-Methylaniline	0.48	N-Benzyl-4-methylaniline	0.29
2-Ethylaniline	0.22	Quinoline	1.86
2,3-Dimethylpyridine	0.01	2-Naphthylamine	0.63
2,4-Dimethylpyridine	0.45	2-Methylquinoline	2.36
2,5-Dimethylaniline	0.22	4-Methylquinoline	3.21
2,6-Dimethylaniline	0.60	6-Methylquinoline	0.44
3,5-Dimethylpyridine	0.04	7-Methylquinoline	1.02
3,5-Dimethylaniline	0.77	8-Methylquinoline	0.33
N,N-Dimethylaniline	0.06	2,4-Dimethylquinoline	5.92
N-Methyl-2-methylaniline	0.16	2,6-Dimethylquinoline	1.95
2,3,5-Trimethylpyridine	0.58	2,7-Dimethylquinoline	1.36
2,4,6-Trimethylpyridine	0.87	2,8-Dimethylquinoline	1.89
3-Ethyl-4-methylpyridine	0.88	3,4-Dimethylquinoline (?)[2]	1.33
4-Ethyl-2-methylpyridine	0.11	4,6-Dimethylquinoline (?)	1.32
5-Ethyl-2-methylpyridine	0.48	2,4,6-Trimethylquinoline	3.41
4-Isopropylpyridine	0.09	2,4,7-Trimethylquinoline	2.85
2,3,4,6-Tetramethylpyridine	0.99	2,4,8-Trimethylquinoline	2.81
2,3,5,6-Tetramethylpyridine	0.24	2,6,8-Trimethylquinoline	2.25
2,6-Dimethyl-4-ethylpyridine	0.45	Acridine (2,3-benzoquinoline)	0.13
3,4-Diethylpyridine (?)	0.63	2,4-Dimethylbenzo[g]quinoline (?)	
2,3-Cyclopentenopyridine	0.16	Phenanthridine (3,4-benzoquinoline)	0.48
Alkyl-5,6,7,8-tetrahydroquinolines (?)		Benzo[f]quinoline (5,6-benzoquinoline)	2.13
2-Phenylpyridine	1.03	Benzo[h]quinoline (7,8-benzoquinoline)	1.64
4-Phenylpyridine	1.21	2,4-Dimethylbenzo[f]quinoline (?)	
2-Methyl-6-phenyl-pyridine (?)	0.72	2,4-Dimethylbenzo[h]quinoline (?)	
Alkylphenylanilines (?)			

[1] The distillable tar bases constitute 0.31 weight-percent of the tar.
[2] (?) indicates uncertainty as to which isomer is present.

TABLE 3. - Displacement chromatographic separation of neutral oil distillate fractions into chemical types

Distillate fraction No.	Weight of charge, g	Column temperature, °C	Saturates + some olefins			Aromatics + some olefins and some O,S compounds			Material retained on column, g	Weight of aromatics identified by GLC, g
			n20D range	Total weight, g	Number of fractions	n20D range	Total weight, g	Number of fractions		
1 + 2[1]	1.77	70	1.3930-1.3941	0.74	5	1.3941-1.5007	0.70	4	0.33	0.57
3[1]	3.15	70	1.4381-1.4832	0.61	3	1.4832-1.5310	2.29	5	0.25	1.95
4[1]	3.60	70	1.4252-1.4471	1.20	4	1.4911-1.5397	2.19	5	0.23	1.66
5[1]	7.40	70	1.4328-1.4695	2.11	7	1.4912-1.5545	4.32	9	0.97	4.30
6[2]	7.70	70	1.4400-1.4683	1.93	5	1.4895-1.5601	5.21	12	0.56	4.81
7 + 8[3]	21	70	1.4025-1.4894	9.98	22	1.4915-1.5658	9.03	11	1.99	5.828
9[2]	4.29	70	1.4281-1.4705	1.77	8	1.4995-1.5867	1.94	7	0.58	1.329
10 + 11[2]	14.93	room temp.	1.4383-1.4938	7.04	18	1.4985-1.5640	6.36	13	1.53	3.152
12 + 13[3]	12.58	room temp.	1.4321-1.4900	5.00	14	1.4990-1.5790	5.87	13	1.71	3.089
14[3]	11.16	room temp.	1.4285-1.4769	5.17	13	1.4991-1.5864	5.24	13	0.75	2.314
15[3]	15.15	room temp.	1.4294-1.4839	6.80	17	1.4971-1.5947	7.31	18	1.04	5.419
16[3]	13.90	room temp.	1.4400-1.4830	4.11	11	1.5027-1.6039	7.81	18	1.98	5.771
17[3]	12.70	room temp.	1.4442-1.4843	2.96	9	1.5001-1.6047	6.97	15	2.77	4.322
18[3]	10.61	room temp.	1.4478-1.5059	3.40	8	1.5331-1.6050	6.14	12	1.07	4.665
19[3]	15.90	room temp.	1.4378-1.4971	6.05	13	1.5083-1.6005	7.13	13	2.72	4.647
20[3]	12.20	70	1.4317-1.5050	5.12	13	1.5219-1.5951	5.06	11	2.02	3.672
21[3]	16.36	70	1.4361-1.5079	6.02	14	1.5179-1.5968	9.11	16	1.23	5.989
22[3]	17.75	70	1.4386-1.5087	5.17	14	1.5218-1.5989	11.22	22	1.36	8.048
23[3]	17.14	70	1.4462-1.4988	3.89	9	1.5283-1.5916	12.24	20	1.01	8.516
24[3]	5.45	70	1.4480-1.5044	1.53	6	1.5449-1.5953	3.52	10	0.40	2.863
25[4]	16.42	85	1.4375-1.4769	2.20	6	1.5115-1.5970	12.73	23	1.49	11.874
26[4]	17.48	85	1.4395-1.4941	2.36	6	1.5228-1.5983	13.50	28	1.62	11.502
27[4]	17.55	85	1.4390-1.5000	2.25	6	1.5195-1.6014	13.59	23	1.71	10.691
28[4]	19.23	90	1.4349-1.4857	2.96	7	1.5100-1.6025	14.58	25	1.69	10.057
29[4]	10.19	90	1.4375-1.4941	2.03	5	1.5251-1.6040	7.00	12	1.16	5.414
30[4]	2.90	95	1.4698	0.40	1	1.5489-1.6015	2.30	6	0.20	1.436
31[4]	7.88	95	1.4572-1.4743	0.93	2	1.5359-1.6027	5.98	11	0.97	4.991
32[4]	5.96	95	1.4509-1.4888	1.42	3	1.5421-1.5998	3.76	7	0.78	2.931
33[4]	7.66	95	1.4537-1.5048	2.01	4	1.5232-1.5978	4.84	8	0.81	2.870
34[4]	8.33	95	1.4591-1.4916	1.13	3	1.5172-1.5960	6.17	11	1.03	3.739
35[4]	6.00	95	1.4587-1.4895	1.40	3	1.5189-1.5903	3.93	6	0.67	2.865
36[4]	5.99	95	1.4555-1.5136	1.64	4	1.5460-1.6009	3.88	8	0.47	2.773
37[4]	8.74	95	1.4565-1.5171	1.66	4	1.5340-1.5982	6.07	12	1.01	3.622
38[4]	8.71	100	1.4570-1.4878	1.46	3	1.5265-1.5938	6.70	14	0.55	
39[4]	8.69	100	1.4551-1.4710	1.26	4	1.5103-1.5951	6.67	13	0.76	
40[4]	8.34	100	1.4457-1.4865	1.58	5	1.5184-1.6000	6.09	13	0.67	
41[4]	8.58	100	1.4391-1.4841	1.88	6	1.5200-1.6008	5.80	14	0.90	
42[4]	8.44	100	1.4392-1.4790	2.22	5	1.5160-1.6052	5.70	14	0.52	
43[4]	8.62	100	1.4390-1.4820	1.98	5	1.5128-1.6065	6.19	17	0.45	
44[4]	8.83	100	1.4473-1.4895	1.50	5	1.5126-1.6112	6.83	20	0.50	
45[4]	3.14	100	1.4495-1.4669	0.49	2	1.5173-1.5851	2.19	8	0.46	

[1] Desorbent: isopropyl alcohol.
[2] Desorbent: butyl alcohol.
[3] Desorbent: isobutyl alcohol.
[4] Desorbent: cyclohexanol.

TABLE 4. - <u>Identification of components producing elution peaks in the
GLC of two aromatic cuts from distillate fractions 10 + 11
and 26</u>

Peak No.	Relative retention at 220°	Compound identified by I.R.	Relative retention of authentic specimen at 220°
1	1.98	Not identified	--
2	2.08	2-Methylnaphthalene	2.10
3	2.29	1-Methylnaphthalene	2.28
4	2.47	Diphenyl ether	2.47
5	2.56	Biphenyl	2.60
6	2.91	2-Ethylnaphthalene	2.93
7	3.18	{ 2,7-Dimethylnaphthalene { 2,6-Dimethylnaphthalene	3.13 3.17
8	3.30	1,7-Dimethylnaphthalene	3.29
9	3.46	{ 1,3-Dimethylnaphthalene { 1,6-Dimethylnaphthalene	3.43 3.43

TABLE 5. - Analysis of individual aromatic hydrocarbons boiling up
to 280° in neutral oil distillate fractions

Compounds identified	Method of identification	Total wt, g	Wt pct in neutral oil[1]
Methylbenzene	Rel. retention	1	Trace
Ethylbenzene	Rel. retention	2	Trace
1,3- and 1,4-Dimethylbenzene	Rel. retention	9	Trace
1,2-Dimethylbenzene	Rel. retention	20	Trace
Isopropylbenzene	Rel. retention	79	Trace
n-Propylbenzene	Rel. retention, I.R.	250	0.002
1-Methyl-3-ethylbenzene.	Rel. retention, I.R.	0.010	0.001
1-Methyl-4-ethylbenzene.	Rel. retention, I.R.	0.0098	0.001
1-Methyl-2-ethylbenzene.	Rel. retention, I.R.	0.0075	0.001
1,2,3-Trimethylbenzene	Rel. retention, I.R.	0.3105	0.045
1,2,4-Trimethylbenzene	Rel. retention, I.R.	0.2695	0.039
1,3,5-Trimethylbenzene	Rel. retention, I.R.	0.1184	0.017
1-Methyl-4-isopropylbenzene	Rel. retention, I.R.	0.0596	0.009
1-Methyl-3-isopropylbenzene	Rel. retention, I.R.	0.0511	0.007
1-Methyl-2-isopropylbenzene	Rel. retention, I.R.	0.0164	0.002
1,2-Diethylbenzene	Rel. retention, I.R.	0.0857	0.012
1,3-Diethylbenzene	Rel. retention, I.R.	0.1009	0.015
1,4-Diethylbenzene	Rel. retention	0.0062	0.001
1,2-Dimethyl-4-ethylbenzene	Rel. retention-bp correlation, I.R.	1.8139	0.260
1,4-Dimethyl-2-ethylbenzene	Rel. retention-bp correlation, I.R.	0.7698	0.110
1,3-Dimethyl-5-ethylbenzene	Rel. retention, I.R.	1.0872	0.156
1,2-Dimethyl-3-ethylbenzene	Rel. retention-bp correlation, I.R.	0.5938	0.085
1-Methyl-3-n-propylbenzene	Rel. retention, I.R.	0.3180	0.046
1-Methyl-2-n-propylbenzene	Rel. retention, I.R.	0.0753	0.011
1,2,4,5-Tetramethylbenzene	Rel. retention, I.R.	1.1066	0.159
1,2,3,5-Tetramethylbenzene	Rel. retention, I.R.	1.7690	0.253
1,2,3,4-Tetramethylbenzene	Rel. retention-bp correlation, I.R.	1.0681	0.153
Indene	Rel. retention, I.R.	0.2331	0.033
3-Methylindene	I.R.	0.7141	0.102
Indan	Rel. retention, I.R.	0.3945	0.057
1-Methylindan	Rel. retention-bp correlation, I.R.	1.1265	0.161
5-Methylindan	Rel. retention-bp correlation, I.R.	1.7566	0.251
4-Methylindan	Rel. retention-bp correlation, I.R.	1.7389	0.249
1,3-Dimethyl-2-n-propylbenzene . . .	Rel. retention-bp correlation	0.0173	0.003
1,2-Dimethyl-3-n-propylbenzene . . .	Rel. retention-bp correlation, I.R.-structural correlation	0.2976	0.042
1,4-Dimethyl-2-n-propylbenzene . . .	Rel. retention-bp correlation, I.R.-structural correlation	0.5974	0.084
1,4-Dimethyl-2-isopropylbenzene . . .	Rel. retention-bp correlation	0.1151	0.017
1-Methyl-3,5-diethylbenzene	Rel. retention, I.R.	0.2393	0.034
1-Methyl-2,4-diethylbenzene	Rel. retention-bp correlation, I.R.-structural correlation	0.9873	0.141
Styrene	I.R.	0.0332	0.005
4-Methylstyrene	I.R.	0.0225	0.003
β-Methylstyrene (trans)	Rel. retention, I.R.	0.1396	0.020
3-Phenyl-1-butene	I.R.	0.1163	0.017
1,2,3,4-Tetrahydronaphthalene	Rel. retention, I.R.	0.6170	0.088
Naphthalene	I.R.	6.3853	0.914

See footnote at end of table.

TABLE 5. - Analysis of individual aromatic hydrocarbons boiling up
to 280° in neutral oil distillate fractions - Continued

Compounds identified	Method of identification	Total wt, g	Wt pct in neutral oil[1]
Benzofuran	Rel. retention, I.R.	0.0991	0.014
5-Methylbenzofuran ⎱ . . . . 6-Methylbenzofuran ⎰	I.R.	0.1432	0.021
2-Methylbenzofuran ⎱ . . . . 3-Methylbenzofuran ⎰	I.R.	0.1681	0.024
7-Methylbenzofuran	I.R.	0.0785	0.011
1,6-Dimethylindan	Rel. retention-bp correlation, I.R.	2.3746	0.340
4,7-Dimethylindan	Rel. retention-bp correlation, I.R.	1.3034	0.186
3-Ethylindene	Rel. retention, I.R.	1.3126	0.188
2-Ethylindene	Rel. retention, I.R.	1.3032	0.186
2,3-Dimethylindene	Rel. retention, I.R.	1.7762	0.254
2-Methyl-1,2,3,4-tetrahydro- naphthalene	I.R.	1.0426	0.149
6-Methyl-1,2,3,4-tetrahydro- naphthalene	I.R.	0.4958	0.071
1-Methylnaphthalene	Rel. retention, I.R.	12.0615	1.728
2-Methylnaphthalene	Rel. retention, I.R.	16.1630	2.315
1-Ethylnaphthalene	Rel. retention, I.R.	1.9777	0.283
2-Ethylnaphthalene	Rel. retention, I.R.	3.1184	0.456
2,7-Dimethylnaphthalene	Rel. retention, I.R.	4.8187	0.690
1,7-Dimethylnaphthalene	Rel. retention, I.R.	4.7915	0.686
2,6-Dimethylnaphthalene	Rel. retention, I.R.	4.1664	0.596
1,6-Dimethylnaphthalene	Rel. retention, I.R.	6.4648	0.926
1,3-Dimethylnaphthalene	Rel. retention, I.R.	6.5617	0.940
2,3-Dimethylnaphthalene	Rel. retention, I.R.	3.8247	0.547
1,5-Dimethylnaphthalene	Rel. retention, I.R.	3.6861	0.528
1,2-Dimethylnaphthalene	Rel. retention, I.R.	3.5632	0.510
1,4-Dimethylnaphthalene	Rel. retention-bp correlation, I.R.	0.0979	0.014
2-Methyl-6-ethylnaphthalene ⎱ . . . . . 2-Methyl-7-ethylnaphthalene ⎰	Rel. retention-bp correlation, U.V. and I.R. -structural correlations	3.9029	0.559
1-Methyl-7-ethylnaphthalene ⎱ and/or . . . . 1-Methyl-6-ethylnaphthalene ⎰	Rel. retention-bp correlation, U.V. and I.R. - structural correlations	3.2925	0.471
1,3,6-Trimethylnaphthalene	Rel. retention-bp correlation, U.V.	0.7338	0.105
1,3,7-Trimethylnaphthalene	Rel. retention, I.R.	0.452	0.064
1,2,6-Trimethylnaphthalene ⎱ . . . . . 1,2,7-Trimethylnaphthalene ⎰	Rel. retention-bp correlation, U.V.	0.8751	--
Biphenyl	Rel. retention, I.R.	18.8235	2.696
4-Methylbiphenyl	Rel. retention, I.R.	0.7271	0.104
3-Methylbiphenyl	Rel. retention, I.R.	1.2431	0.178
Cyclohexyl benzene	Rel. retention, I.R.	0.2769	0.039
2a,3,4,5-Tetrahydroacenaphthene . .	Rel. retention, I.R.	1.1713	0.167
Acenaphthylene	Rel. retention, I.R.	0.6963	0.099
Acenaphthene	Rel. retention, I.R.	2.336	--
Diphenyl ether	Rel. retention, I.R.	38.5897	5.528
2,3-Dimethylbenzofuran	I.R. -structural correlation	0.1778	0.025
Dimethylbenzofuran II	I.R. -structural correlation	1.7848	0.255
Dimethylbenzofuran III	I.R. -structural correlation	0.6451	0.092
Dibenzofuran	Rel. retention, I.R.	1.4718	--

[1] Total neutral oil distilling up to about 360°, representing 16.92 weight-percent of the total tar.

TABLE 6. - Analysis of individual C_{10}-C_{16} n-paraffins, isoparaffins
and α-olefins in neutral oil distillate fractions

Compounds identified	Method of identification	Total wt., g	Wt pct in neutral oil[1]
n-Decane	Rel. retention, I.R.	0.2481	0.036
n-Undecane	Rel. retention, I.R.	1.4842	0.213
n-Dodecane	Rel. retention, I.R.	6.6226	0.949
n-Tridecane	Rel. retention, I.R.	11.2807	1.62
n-Tetradecane	Rel. retention, I.R.	5.5026	0.788
n-Pentadecane	Rel. retention, I.R.	7.3638	1.06
n-Hexadecane	Rel. retention, I.R.	3.7244	0.534
		Total	5.200
2-Methyl nonane	Bp and I.R.-structural correlation	0.1551	0.022
2-Methyl decane	Rel. retention, I.R.	0.2356	0.034
2-Methyl undecane	Bp and I.R.-structural correlation	0.8742	0.125
2-Methyl dodecane	Bp and I.R.-structural correlation	1.4344	0.206
2-Methyl tridecane	Bp and I.R.-structural correlation	1.4000	0.201
2-Methyl tetradecane	Bp and I.R.-structural correlation	2.9188	0.418
2-Methyl pentadecane	Bp and I.R.-structural correlation	0.1367	0.020
		Total	1.026
1-Decene	Rel. retention, I.R.	0.1595	0.023
1-Undecene	Rel. retention, I.R.	1.1871	0.170
1-Dodecene	Rel. retention, I.R.	1.4485	0.208
1-Tridecene	Rel. retention, I.R.	4.5744	0.655
1-Tetradecene	Rel. retention, I.R.	4.3582	0.624
1-Pentadecene	Rel. retention, I.R.	2.8693	0.411
1-Hexadecene	Rel. retention, I.R.	2.1243	0.304
		Total	2.395

[1] Total neutral oil distilling up to about 360°, representing 16.92 weight-percent of the total tar.

TABLE 7. - <u>Physical properties and other data for resins from low-temperature coal tars</u>

Resin No.	Source	Extraction scheme		Yield, weight percent[1]	Molecular weight, M
		Soluble in:	Insoluble in:		
1 A	Bituminous	quinoline	benzene	4.3	628
1 B	pitch	benzene	pet. ether[2]	64.8	383
2 A	Lignite	quinoline	benzene	1.7	510
2 B	tar	benzene	pet. ether[2]	22.5	391
3 A	Subbituminous	quinoline	benzene	18.3	603
3 B	pitch	benzene	pet. ether[2]	40.1	482
4 B	Subbituminous	benzene[3]	pet. ether[2]	35.8	476[4]
4 B'	pitch				410[5]

Resin No.	Density, d_4^{20}		Refractive index,[6] n_D^{20}	Weight percent		
	As a "solid"	From pyridine solutions		C	H	O[7]
1 A	1.326	1.326	1.694	76.3	5.3	15.3
1 B	1.129	1.130	1.642	84.3	7.5	6.3
2 A	1.255	--	1.669	81.9	4.3	9.5
2 B	1.155	1.154	1.641	79.4	7.2	11.9
3 A	1.261	1.259	1.669	76.0	5.9	13.5
3 B	1.201	1.200	1.653	78.5	6.7	14.3
4 B	1.159	1.156	1.653	78.8	7.4	10.6
4 B'	1.140	1.141	1.639	81.1	7.8	10.2

[1] On the basis of the specified source.
[2] Petroleum ether, boiling range 100° to 115°C.
[3] Ratio of solvent to pitch for these two resins: benzene 4 to 1, petroleum ether 20 to 1; ratios for all other resins 25 to 1.
[4] Powdery fraction.
[5] Semi-solid fraction.
[6] From pyridine solutions.
[7] By direct oxygen determination.

TABLE 8. - Number and arrangement of rings in low-temperature tar resins

Resin No.	Ring analysis			Approximate average molecular formula[1]	Corrected[2]		Series	Ring arrangement
	R_T	R_A	R_N		R/C	H/C		Representative hydrocarbon[3]
1 A	12.6	5.5	7.1	$C_{40}H_{33}O_6$	0.27	0.99	VII	Octadecahydrodiphenanthrocoronene
1 B	5.4	3.8	1.6	$C_{27}H_{29}O_2$	0.19	1.11	I	Hexahydroheptamethylpicene
2 A	10.1	4.1	6.0	$C_{35}H_{22}O_3$	0.27	0.74	VII	Octahydromethylbenzonaphthocoronene
2 B	4.6	3.8	0.8	$C_{28}H_{28}O_2$	0.16	1.18	I	Tetrahydroheptamethylpicene
3 A	10.3	5.1	5.2	$C_{28}H_{36}O_5$	0.24	1.06	VII	Hexadecahydrohexamethylbenzonaphthocoronene
3 B	6.2	4.5	1.7	$C_{32}H_{32}O_4$	0.17	1.14	I	Tetrahydrodecamethylbenzopicene
4 B	5.8	5.0	0.8	$C_{31}H_{35}O_3$	0.17	1.21	I	Octahydrooctamethylbenzopicene
4 B'	4.9	4.0	0.9	$C_{28}H_{32}O_3$	0.16	1.23	I	Tetrahydrononamethylpicene

[1] Smaller amounts of nitrogen and sulfur not included.

[2] Corrected for oxygen only.

[3] Picene is given as an example of a linear ring arrangement in Series I; coronene is given as an example of a globular ring arrangement in Series VII; all oxygen atoms, including phenolic oxygen and heterocyclic oxygen, in the resin are rendered as CH_2 groups in these representative hydrocarbons.

TABLE 9. - Relative retentions and infrared absorption bands of pyrolysis products from a subbituminous coal tar resin

Compound	Relative retention[1]		GLC peak No.	Some observed I.R. bands, wavelength, μ	Weight-percent[2]
	Pure	Pyrolysis product			
Methane	0.37	0.37	1		
		0.43	2		
		0.49	3		
		0.57	4		
1-Pentene[3]	0.60	0.59	5		9.7
2-Methyl-1-pentene[3]	0.70	0.71	6		2.7
2,2,4-Trimethylpentane	0.93	0.93	7	7.33, 7.90, 8.03, 8.32, 8.57, 10.21,	24.7
Benzene	1.00	1.00	8	2.44, 3.20, 3.25, 5.12, 5.52, 9.65, 14.85	19.3
2,3,4-Trimethylpentane	1.15	1.15	9	7.25, 7.32, 8.93, 9.30, 10.07, 10.32, 10.92	26.9
2,2,4-Tetramethylpentane	1.23	1.23	10	8.03, 8.54, 10.28	7.0
Toluene	1.37	1.37	11	9.28, 9.71, 13.74, 14.43	3.5
2,6-Dimethyl-1,4-heptadiene[3]	1.53[4]	1.55	12		0.5
p-Xylene	1.92	1.93	13	8.95, 12.60 (para)	0.9
m-Xylene				8.57, 9.13, 13.02, 14.53 (meta)	2.1
o-Xylene	2.14	2.15	14	7.22, 8.96, 9.53, 9.81, 13.46	2.7
					100.0

[1] Relative to benzene on Apiezon L grease at 220°C.
[2] On the basis of the total liquid pyrolysis products.
[3] This compound is typical of several equally likely possibilities.
[4] Retention obtained from log retention-boiling point correlations.

TABLE 10.- Relative retentions and infrared absorption bands of
pyrolysis products from a bituminous coal tar resin

| Compound | Relative retention[1] | | GLC peak No. | Some observed I.R. bands, wavelength, μ | | Weight-percent |
	Pure	Pyrolysis product		Pure	Resin	
Methane	0.37	0.37	1			4.1
		0.57	2			
		0.59	3			
		0.62	4			
2-Methylpentane	0.70	0.73	5	8.53, 8.70, 13.51	8.55, 8.72, 13.56	16.0
2,2,4-Trimethylpentane	0.94	0.95	6	7.33, 7.81, 8.03, 8.32, 8.58, 10.22	7.33, 7.81, 8.03, 8.32, 8.58, 10.23	
Benzene	1.00	1.00	7	2.44, 5.12, 5.52, 9.68, 14.85	2.44, 5.12, 5.52, 9.68, 14.88	32.9
2,3,4-Trimethylpentane	1.15	1.17	8	7.23, 7.30, 8.93, 9.31, 10.05, 10.29, 10.92	7.25, 7.33, 8.94, 9.32, 10.06, 10.32, 10.93	26.6
2,3,3-Trimethylpentane[2]	1.19			9.20, 9.95, 12.88[3]	9.22, 9.97, 12.93	3.0
2,2,4,4-Tetramethylpentane	1.25	1.26	9	8.05, 8.55, 10.28, 10.93	8.05, 8.55, 10.30, 10.94	7.0
Toluene	1.37	1.39	10	9.26, 9.70, 13.74, 14.43	9.28, 9.72, 13.79, 14.48	5.9
2,2,3,4-Tetramethylpentane[2]	1.54	1.57	11	8.33, 8.98, 9.22[3]	8.34, 9.00, 9.24	2.3
p-Xylene				8.93, 12.57	8.95, 12.61 (para)	1.2
m-Xylene	1.92	1.94	12	8.54, 9.13, 13.01, 14.50	8.55, 9.14, 13.04, 14.54 (meta)	0.4
o-Xylene	2.14	2.17	13	8.95, 9.78, 13.47	8.96, 9.80, 13.50 (ortho)	0.6
						100.0

[1] Relative to benzene on Apiezon L grease at 220°C.

[2] Retention obtained from log retention-boiling point correlations.

[3] Bands obtained from A.P.I. Project 44 spectra.

TABLE 11. - Comparison of relative amounts of pyrolysis
products from bituminous and subbituminous
coal tar resins

Compound	Weights relative to 2,3,4-trimethylpentane	
	Bituminous	Subbituminous
1-Pentene	....	0.36
2-Methylpentane	0.15	....
2-Methyl-1-pentene	....	0.10
2,2,4-Trimethylpentane	0.60	0.92
Benzene	1.23	0.72
2,3,4-Trimethylpentane	1.00	1.00
2,3,3-Trimethylpentane	0.11	....
2,2,4,4-Tetramethylpentane ..	0.26	0.26
Toluene	0.22	0.13
2,2,3,4-Tetramethylpentane ..	0.09	....
2,6-Dimethyl-1,4-heptadiene ..	....	0.02
p-Xylene	0.04	0.03
m-Xylene	0.01	0.08
o-Xylene	0.02	0.10

Figure 1. - Chromatogram of Tar Acids From Tar
Distillate.
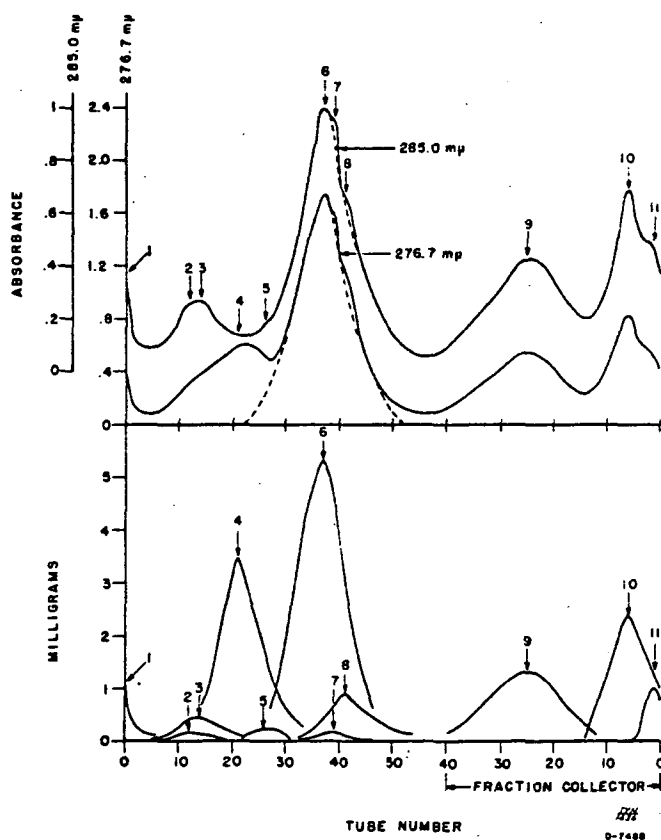
Figure 2. - Countercurrent Distribution of Tar Acids
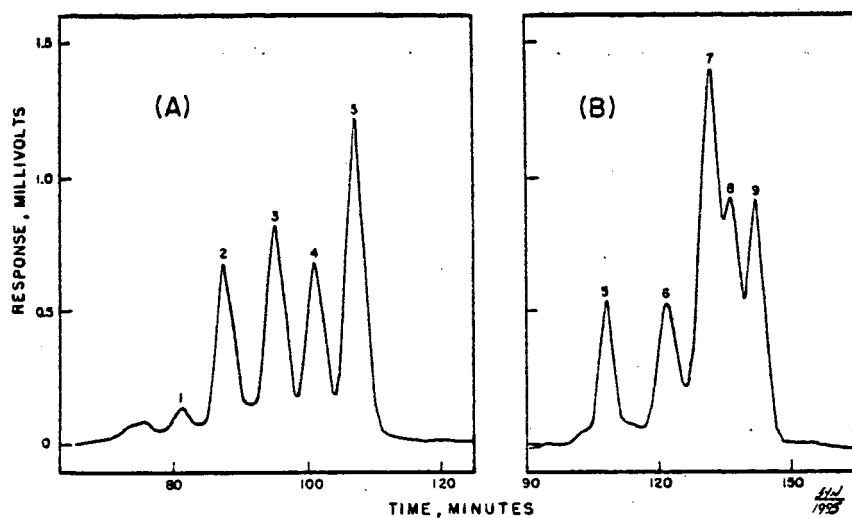Boiling 238°-251°C; 100 Transfers;
pH 11.58.

Figure 3. - Chromatograms of Two Aromatic Cuts
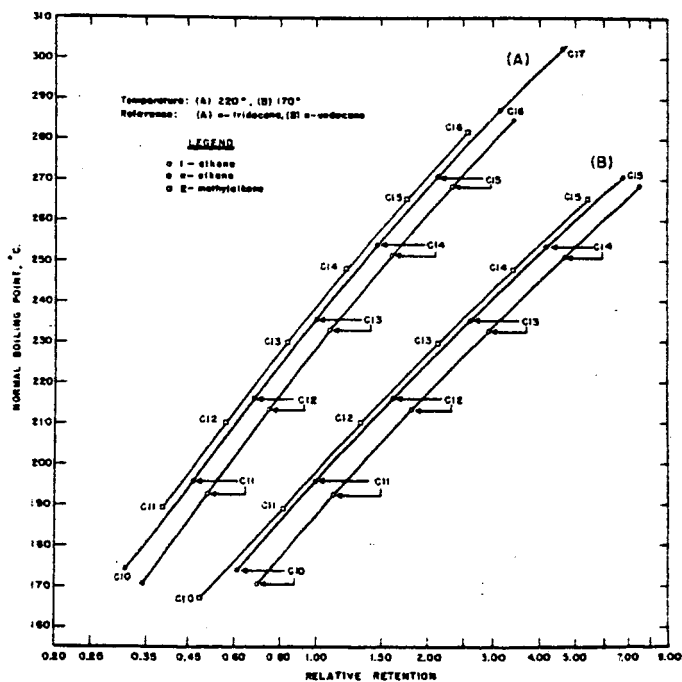Obtained From Distillate Fractions 10 +
11 (A) and 26 (B).

Figure 4. - Correlations Between Boiling Points and
Relative Retentions of C_{10}-C_{16} n-Paraffins,
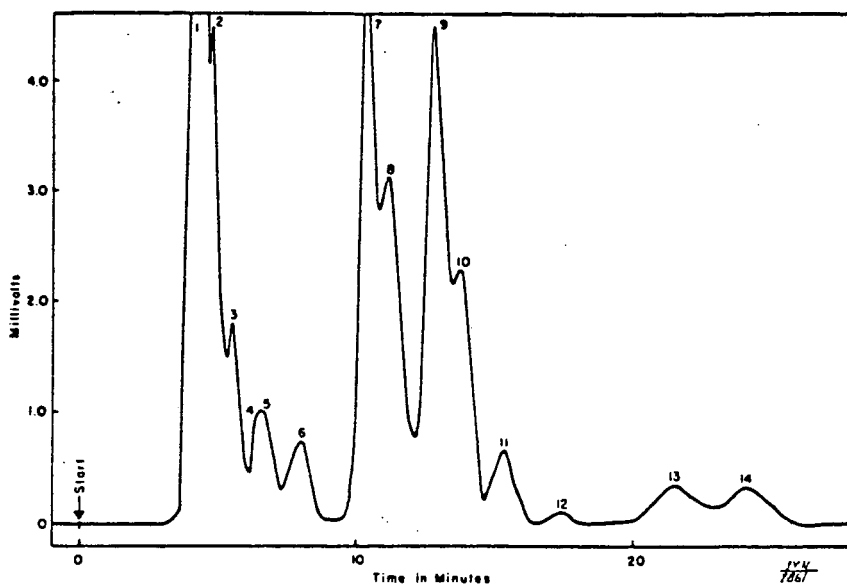Isoparaffins and α-Olefins on Polyphenyl
Ether.

Figure 5. - Chromatogram of Pyrolysis Products From
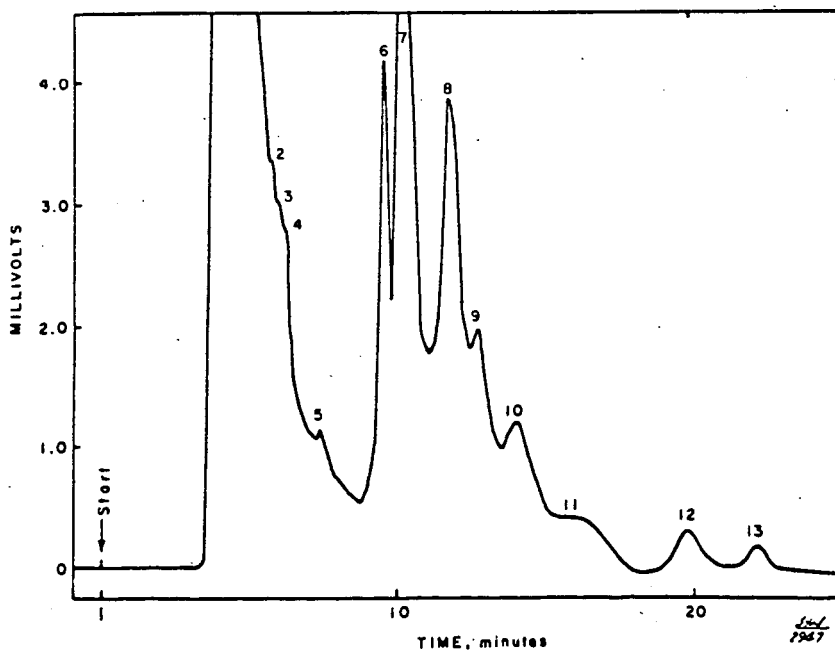a Subbituminous Coal Tar Resin.

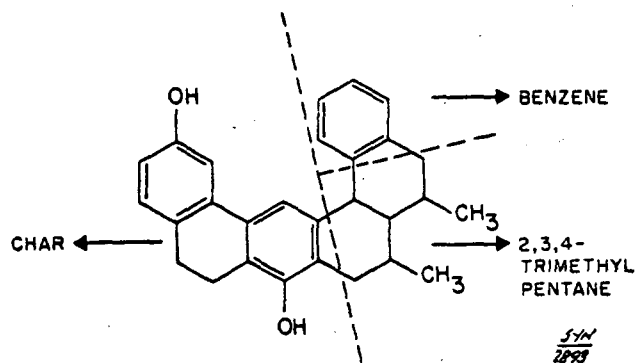Figure 6. - Chromatogram of Pyrolysis Products From
a Bituminous Coal Tar Resin.

Figure 7. - A Representation of the Pyrolysis
of a Hypothetical Resin Molecule.